SYNOPSIS OF THE Ph.D. THESIS

Magnetic, Optical and Electrical properties of doped SnO_2 and ZnO nanostructures: Sol-gel and Hydrothermal synthesis

SUBMITTED BY

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❖ Introduction

In recent years, there has been extensive interest of researchers in the diluted magnetic semiconductors (DMSs) for their promising applications in spintronics, nanoelectronics, nanophotonics and microwave devices that allow the control of both the spin and the charge carriers [1]. Thus, such type of materials will be capable of integrating the electronics, magnetism, and optical functionalities in a single material, leading to low cost, high-speed, and small sized devices operating at very low power. Wide band gap oxide based DMSs such as ZnO, SnO_2, TiO_2 and HfO_2 have attracted considerable attention whenever doped with transition metal (TM) ions (Co, Mn, Ni, Fe, Cr, etc.) [2,3]. This is because of their remarkable electronic, optical and magnetic properties, resulting from large sp-d exchange interactions between the magnetic ions and the band electrons. These DMSs have stimulated several experimental groups, which resulted in the production of magnetic semiconductors in various host semiconductor materials by doping with 3*d* transition metals. For most of the experimental results, doubts arose about the real origin of ferromagnetism (FM). Some researchers demonstrated that the ferromagnetism is due to segregation of metallic clusters while in some other studies it is reported, because of the transition metal elements with different valence states. Though, it was also observed that the host material itself (without any magnetic element doping) becomes magnetic when the size of the crystallites is in nanometers [4]. In many reports, DMSs doped with transition metal (TM) ions showed an effective route to obtain room-temperature ferromagnetism in ZnO [5] and SnO_2 [6] systems.

Among the oxide based DMS materials, SnO_2 exhibits remarkable behavior because of native oxygen vacancies, high carrier density and transparency and excellent chemical and thermal stabilities. In current studies, SnO_2 based photocatalysts are the most promising photocatalysts due to their high oxidative efficiency, photochemical stability and low-cost [7]. As most DMS ferromagnetism is thought to involve electrons or holes mediating long-range interaction between dopants, the native oxygen vacancies and high carrier density. Tailoring the physical properties and adding new functionalities to the existing semiconductors by altering the structure, composition and grain size are new approaches in advancing the current application of semiconductor materials. It has been found experimentally that the preparation of these materials in the nanoscale range increases the surface-to-volume ratio which may affect the structural and most physical properties. Recent research has been devoted to the synthesis of SnO_2 nanostructures with Co and Fe doping which displayed room temperature ferromagnetism of nanomaterial with varying dopant concentrations [8]. Ferromagnetism in ceramic $Sn_{0.95}Fe_{0.05}O_2$ with a magnetic moment of $0.95\mu_B$/Fe, ~85% of the iron being in magnetically ordered high-spin Fe^{3+} and a Curie temperature of about 360 K, have been reported by Fitzgerald et al. [9]. On the other hand, Punnoose *et al.* [10] reported paramagnetic behavior in a chemically synthesized $Sn_{0.95}Fe_{0.05}O_2$ powder sample prepared above at 600^0C, while Adhikari *et al.* [11]

observed antiferromagnetic behavior of 5% Fe-doped SnO_2 nanoparticles synthesized by a chemical co-precipitation method. Overall, the origin of ferromagnetism in TM doped SnO_2 system is controversial and more detailed investigations are required.

Another diluted magnetic semiconductor (DMS) zinc oxide (ZnO), has gained substantial interest in the research community because of its wide band gap (3.37 eV) and large exciton binding energy (60 meV) which lead to lasing action based on exciton recombination even above room temperature and useful in fabricating many microelectronic and optoelectronic devices [12, 13]. As among the functional oxides of perovskite, rutile, CaF_2, spinel, and wurtzite structures, zinc oxide (ZnO) is unique because it exhibits dual semiconducting and piezoelectric properties [12]. Moreover, ZnO is a kind of semiconducting material which has diverse structures and their configurations are much richer than any other nanomaterial. The field is also fueled by theoretical predictions and perhaps experimental confirmation of ferromagnetism at room temperature for potential spintronics applications. Even though research focusing on ZnO goes back many decades, the investigations of obtaining room temperature ferromagnetic semiconductor materials by adding metal impurities into ZnO became intense since Dietl *et al.* [14] used a simple theory to predict that room temperature ferromagnetic semiconductors might be created by substituting iron and cobalt ions in wide band gap semiconductors like ZnO [15]. As a typical transition metal, Fe ion has been selected to dope into ZnO to get DMSs. Up to now, the ferromagnetism in Fe-doped ZnO is still in dispute. It is reported that several Fe-doped ZnO DMSs displayed ferromagnetism at low temperature and revealed paramagnetism at room temperature [16], while in other cases, room temperature ferromagnetism (RTFM) was obtained in Fe-doped ZnO DMSs [17]. In recent years, it has been established that ferromagnetic properties in doped ZnO system can be enhanced through doping with transition metal ions [18]. Therefore, investigation of RTFM in ZnO with Fe and Co doping will be focused in this work.

The literature survey indicates that the nanometric size has great impact on the performance of several material systems which may affect various physical properties of the host semiconductors and the DMS materials derived from them. For example, when the crystallite size of some of the DMS materials is reduced to below 20 nm, they are found to exhibit better ferromagnetic properties when compared with those having nanocrystalline particles (>100 nm) . Apart from this, nanocrystalline oxide DMS materials may be exploited for a variety of applications such as spintronics devices, biomedical applications, magnetic storage devices, ferrofluids, etc. Therefore, it is important to study the influence of nanometric size on various physical properties of oxide based diluted magnetic semiconductors.

Moreover, there are just few reports on the optical properties of semiconductors SnO_2 and ZnO based nano material doped with luminescence centers such as transition metals and co-doped with rare earth ions which exhibit efficient luminescence even at room temperature. Though we know that, the rare earth ions (Ce, Eu, Gd and La) are good luminescence centers due to their narrow and intense emission lines originating

from 4f intra shell transitions. Even the rare earth oxides are found to have polymorph, good thermal stability, etc. due to their *f* electron and multi-electron configuration. Moreover, the controlled synthesis of ceria-based nanomaterial with pure phase, desirable composition, uniform morphology and tuneable surfaces has gained importance, since these materials exhibit unique properties when their sizes are reduced to nanometre scale. For example, the band gap of nano-ceria increases, concomitant the blue-shifting appearing in the adsorption spectra owing to the quantum size effect. Some studies have also reported that doping of cerium and lanthanum enhances the dielectric response and *ac* conductivity of metal oxide semiconductors. Furthermore, it must also be considered that the introduction of rare earth ions (usually trivalent cations) influences the material's electronic distribution, favoring, for instance, the adsorption of oxygen species and resulting in materials with suitable morphological characteristics (high surface area, small particles, etc.). [19] Thus, the rare earth doped nanostructures have wide variety of applications including phosphors, display monitors, x-ray imaging, scintillators, optical communications and fluorescence imaging. So the synthesis of transition metal ions (Co and Fe) doped and rare earth ions (Ce and La) co-doped DMS SnO_2 and ZnO nanostructures will remain a major task of the present investigation.

Several methods used by researchers to prepare nanostructures of DMS SnO_2 and ZnO are chemical co-precipitation, wet chemical route, chemical vapor deposition, microemulsion, solvothermal, sol-gel and hydrothermal processing [20]. However, most of them have been directed towards the preparation of nanostructures with a large grain size distribution in the range of a few micrometers, despite complicated experimental steps and high reaction temperatures. Therefore, in view of the above discussion, the main aim of the research work has been to prepare nanostructures of DMS SnO_2 and ZnO by the simplest, eco- friendly and economic chemical routes. Moreover the present investigation focused on the processing parameters, the effects of variation of dopant concentration of transition metal ions of cobalt and iron on SnO_2 and ZnO, and the incorporation of rare earth ions of cerium and lanthanum and their effects on the morphological, crystallographic, optical, magnetic and electrical characteristics of the synthesized samples.

❖ Objectives:

1. To synthesize pure and doped (Dopants: transition metals and rare earth elements) SnO_2 and ZnO nanostructures by chemical route similar to sol-gel using polyvinyl alcohol (PVA) as a surfactant and by hydrothermal method.
2. To study the morphological and crystallographic characteristics of the synthesized materials.
3. To investigate the optical characteristics of the synthesized nanomaterial.
4. To examine the magnetic and electrical behavior of the prepared nanostructures.

❖ Significance of the research work:

In the present research work, the focus is on the synthesis of DMS based nanomaterial of SnO_2 and ZnO by two different techniques (sol-gel and hydrothermal method) and comparison of the results of the samples prepared by above mentioned methods by considering various compositions. The effect of incorporation of transition metal ions (Co and Fe) as dopants and rare earth ions (Ce and La) as co-dopants in the SnO_2 and ZnO host lattice has also been studied. The morphological, structural, magnetic, optical and electrical properties have been investigated in detail. There is no such detailed comparative study of these DMS materials, reported so far. Further, these results can be useful to a large extent in giving new dimensions to the emerging spintronic and optoelectronic technology.

❖ Methodology:

For the synthesis of pure and transition metals doped and rare earth elements co-doped SnO_2 and ZnO nanostructures, two methods have been used as sol-gel and hydrothermal routes. The results of the samples prepared by the two techniques would be compared.

1. Synthesis of pure and transition metals doped and rare earth elements co-doped SnO_2 and ZnO nanostructures by chemical route similar to sol-gel using polyvinyl alcohol (PVA) as a surfactant and by hydrothermal method. The following series of SnO_2 nanostructures have been prepared by sol-gel and hydrothermal method respectively:

(i) $Sn_{1-x}Co_xO_2$ and $Sn_{1-x}Fe_xO_2$ nanostructures (x = 0, 0.01, 0.03, 0.05) by sol-gel method.

(ii) $Sn_{0.91}Co_{0.05}R_{0.04}O_2$ and $Sn_{0.91}Feo_{0.05}R_{0.04}O_2$ (R = Ce and La) by sol-gel method.

(iii) $Sn_{0.95}Co_{0.05}O_2$ nanostructures at constant temperature, with varying heating time t = 15h, 30h and 45h and pH has been maintained as required, by hydrothermal method.

(iv) $Zn_{1-x}Co_xO$ and $Zn_{1-x}Fe_xO$ nanostructures (x = 0, 0.01, 0.03, 0.05) by sol-gel method.

(v) $Zn_{0.91}Co_{0.05}R_{0.04}O$ and $Zn_{0.91}Feo_{0.05}R_{0.04}O$ (R = Ce and La) by sol-gel method.

(vi) $Zn_{0.95}Co_{0.05}O$ nanostructures at constant temperature, with varying heating time t = 15h, 30h and 45h and pH has been maintained as required, by hydrothermal technique.

In the above series of samples, the host lattice SnO_2 and ZnO was doped with transition metal ions (Co and Fe) and co-doped with rare earth ions (Ce and La).

Processing steps for the above samples:

(A) Synthesis by chemical route similar to sol-gel method:

(i) Samples of different chemical constituents have been taken in the stoichiometric ratio as defined above.

(ii) Crystallization of powder samples.

(iii) Annealing of samples.

(iv) Pressing of crystalline powder to get in pellet form.

(v) Sintering the pellets.

(vi) Characterization of powder samples and pellets.

(B) Synthesis by Hydrothermal technique:

(vii) Samples of different chemical constituents have been taken in the stoichiometric ratio as defined above.

(viii) Crystallization of powder samples.

(ix) Pressing of crystalline powder to get in pellet form.

(x) Sintering of the pellets.

(xi) Characterization of powder samples and pellets.

All the series of the samples have been prepared at the Akal School of Physics, Eternal University, Baru Sahib, H.P and characterization was done at SAIF Panjab University, Chandigarh, USIC, University of Delhi, Delhi and National Physical Laboratory, New Delhi.

2. Study of morphological and crystallographic characteristics of the synthesized materials. The following characterization techniques have been used.

(i) X- ray diffraction

(ii) Transmission electron microscopy

(iii) Scanning electron microscopy

(iv) Raman spectroscopy

(v) X- ray photoelectron spectroscopy

X-ray diffraction of different samples has been studied by X-Pert PRO PANalytical system. The microstructural properties have been investigated by scanning electron microscopy using JEOL JSM 6100, Transmission electron microscopy has been performed using Hitachi H-7500 at SAIF Panjab University, Chandigarh. Scanning electron microscopy (SEM) images have been observed using JEOL JSM6100 system. Raman spectra has been recorded on Renishaw UK which consists of Ar ion laser with 518 nm wavelength and 50 mW power at USIC, University of Delhi, Delhi. The photoemission spectrum has been recorded using a VSW photoelectron spectrometer at NPL New Delhi for XPS studies.

3. Investigation of the optical characteristics of the synthesized nanostructures. The following characterization techniques have been used.

(i) Fourier Transform Infrared spectroscopy (FTIR)

(ii) UV-Visible spectroscopy

(iii) Raman spectroscopy

(iv) Photoluminescence

Fourier transform infrared spectrum has been recorded on a Perkin Elmer spectrum 400 FT-IR/FT-FIR spectrometer using triglyceride (TGS) detector. The optical absorbance spectrum was measured using Perkin Elmer λ 35 spectrophotometer at University of Delhi, Delhi. Photoluminescence and Raman spectra have been recorded on Renishaw UK which consists of Ar ion laser with 518 nm wavelength and 50 mW power at USIC, University of Delhi, Delhi.

4. Examination of magnetic and electrical behavior of synthesized nanostructures. The following characterization techniques have been used.

Magnetic properties:

(i) Saturation magnetization

(ii) Coercivity

(iii) Phase transition temperature

Magnetic measurements have been performed at room temperature using a vibrating sample magnetometer (VSM-735) at NPL, New Delhi.

Electrical properties:

(i) Dielectric constant

(ii) Loss tangent

(iii) AC electrical conductivity

The electrical measurements have been performed at room temperature using an impedance analyzer (4200 semiconductor character unit, CVU module) at University of Delhi, Delhi. For electrical measurements, the annealed powder has been pressed into pellets of thickness ~ 0.5 mm by cold isotatic pressing method with a pressure of 5 bar for 5 min and then sintered.

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Synopsis is recommended for acceptance by the Eternal University

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Recommendation _____

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